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<b>(21) International Application Number:</b> PCT/US90/03077 <b>(22) International Filing Date:</b> 7 June 1990 (07.06.90)  <b>(30) Priority data:</b> 371,138                      26 June 1989 (26.06.89)                      US  <b>(71) Applicant:</b> E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).  <b>(72) Inventor:</b> WHELAND, Robert, Clayton ; 510 Twaddell Mill Road, Wilmington, DE 19807 (US).  <b>(74) Agents:</b> SIEGELL, Barbara, C. et al.; E.I. du Pont de Nemours and Company, Legal Department, 1007 Market Street, Wilmington, DE 19898 (US).		<b>(81) Designated States:</b> AT (European patent), BE (European patent), CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> POLY(PERFLUOROETHER)ACYL PEROXIDES  <b>(57) Abstract</b>  This invention concerns novel polymeric perfluoroether acyl peroxides and an improved process for making them.		

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TITLE

## POLY(PERFLUOROETHER)ACYL PEROXIDES

5

BACKGROUND OF THE INVENTION1. Field of the Invention

This invention concerns polymeric perfluoro-  
etheracyl peroxides, and an improved process for  
10 making them.

Selected high molecular weight fluorocarbon and  
perfluoroether peroxides have been known in the art  
for a number of years. The synthesis of these  
compounds has generally involved the reaction of  
15 aqueous peroxide with an acid halide. Using this  
method, some of the acid halide is converted to  
carboxylate salt. As the molecular weight of the  
carboxylate salt increases, soaps and stiff  
emulsified gels are formed that interfere with the  
20 isolation of the pure compound. Conventional methods  
of isolating the peroxide have involved treatment of  
the mixture with sulfuric acid and following up the  
procedure with centrifugation to separate out the  
peroxide. See, e.g., U.S. Patent 3,882,193. The  
25 present invention improves upon prior art procedures  
for synthesizing oligomeric peroxides by limiting the  
presence of water so as to retard emulsion and gel  
formation and result in the direct formation of a  
liquid product containing the high molecular weight  
30 perfluoroether peroxides. This invention also  
concerns novel polymeric peroxides produced by the  
present process, and a novel method of coating  
substrates with fluoropolymers using the polymeric  
peroxides.

35

2. Discussion of the Prior Art

U.S. Patents 2,559,630 and 2,792,423 disclose  
polymeric perfluoroalkylacyl peroxides and a method

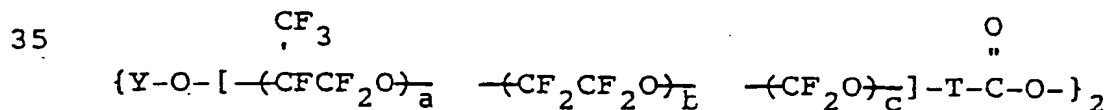
for making them. The chemistry used in the process to produce the acyl peroxides is the reaction of the corresponding acyl halide (usually fluoride or chloride) with a peroxide under basic conditions. The peroxide can be added as hydrogen peroxide and a base such as sodium hydroxide added, or the base and peroxide can be combined in one compound such as sodium peroxide. The reaction is often done in a heterogeneous system containing water to dissolve the inorganic salts, and an organic solvent to dissolve the perfluoro polymer.

U.S. Patents 3,810,875 and 3,882,193 disclose polymeric perfluoroether acyl peroxides wherein both ends of the perfluoroether polymers end in peroxides, and each "block" of perfluoroether polymer is part of a larger polymer molecule joined by peroxide linkages. Thus, such poly(perfluoroether)acyl peroxides are "difunctional", that is reactive on both ends of the perfluoroether blocks. The same basic chemistry described above was used to prepare the peroxides.

Z. Chengxue et al., in Journal of Organic Chemistry, vol. 1982, pages 2009-2013 describe the decomposition of perfluoroacyl peroxides for both perfluorocarbon and perfluoroether compounds, but the molecular weights of the perfluoro segments are very low.

### SUMMARY OF THE INVENTION

A poly(perfluoroether)acyl peroxide of the formula



wherein

5 Y is a perfluoroalkyl group containing up to 12 carbon atoms,  $a+b+c$  is a minimum of 2 and a maximum such that the maximum molecular weight of the peroxide is about 33,000; and

T is  $-\text{CF}_2-$  and  $-\text{CF}(\text{CF}_3)-$ ,  
10 provided that when a is zero, T is not  $-\text{CF}(\text{CF}_3)-$ , when b is zero T is not  $-\text{CF}_2-$ , and further provided that when a and b are both zero, T is  $-\text{CF}_2-$ .

Also provided is an improved process for the preparation of such peroxides from the corresponding poly(perfluoroether)acyl halide, peroxide and base,  
15 the improvement consisting of using a specified amount of water in the reaction. The molar ratio of water/peroxide (starting material) present in the reaction ranges from about 0.2 to about 10. An optional improvement consists of passing the reaction  
20 mixture at the conclusion of the reaction through a solid desiccant to remove liquid water.

Also provided is a process for the coating of substrates with fluoropolymers using such peroxides as the initiators. The peroxide is coated on the  
25 substrate, as by evaporation of a solution of the peroxide on the substrate, and then the peroxide coated substrate is exposed to fluorine containing monomers capable of being polymerized by free radicals, at a temperature at which the peroxide  
30 decomposes.

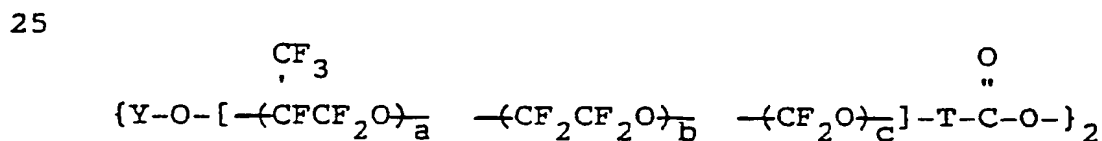
#### DETAILS OF THE INVENTION

It is known that poly(perfluoroethers) tend to be liquids, and it is the object of this invention to  
35 provide liquid, easily used, poly(perfluoroether)acyl

peroxides that can be used, for example, to place relatively large poly(perfluoroether) groups (blocks)  
 5 on the ends of free radical polymerized polymers.

Poly(perfluoroether)acyl peroxides are commonly made by reacting a poly(perfluoroether)acyl halide, usually the fluoride or chloride, with an inorganic peroxide in the presence of base. This is usually  
 10 done in the presence of water, to dissolve the inorganic reagents, and an organic solvent, to dissolve the poly(perfluoroether)acyl halide. An inevitable consequence of this reaction is the production of at least small amounts of  
 15 poly(perfluoroether) carboxylate. When the perfluoroether chain is of substantial length, this acts as a surfactant, causing the formation of virtually intractable emulsions and suspensions, which greatly complicates isolation of the peroxide  
 20 and reduces the yield obtained. It is a further objective of this invention to provide a process for making such peroxides.

The poly(perfluoroether)acyl peroxides of this invention have the formula



wherein

30 Y is a perfluoroalkyl group containing up to 12 carbon atoms, a+b+c is a minimum of 2 and a maximum such that the maximum molecular weight of the peroxide is about 33,000; and

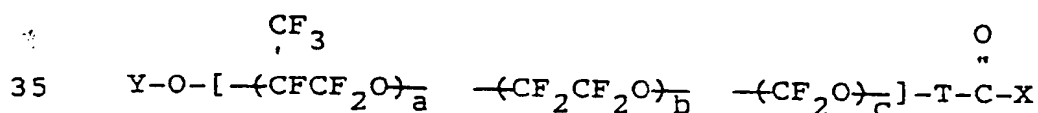
T is -CF<sub>2</sub>- and -CF(CF<sub>3</sub>)-, provided that when a is zero, T is not -CF(CF<sub>3</sub>)-, when b is zero T is not -CF<sub>2</sub>-, and further provided  
 35 that when a and b are both zero, T is -CF<sub>2</sub>-.

It is understood that within the bracketed term "[ ]", if more than one monomer is used, the polymer may be a random copolymer or a block copolymer; if it is a block copolymer, then T will be a fragment of the last monomer used. This is also true for the poly(perfluoroether)acyl halide precursor (infra).

Y is an end group derived from the species that initiated the polymerization of the perfluoroether. Most typically, and preferred, it is  $\text{CF}_3$ - when carbonyl fluoride ( $\text{COF}_2$ ) is the monomer (repeat unit),  $\text{CF}_3\text{CF}_2$ - when tetrafluoroethylene oxide is the monomer (repeat unit), and  $\text{CF}_3\text{CF}_2\text{CF}_2$ - when hexafluoropropylene oxide is the monomer (repeat unit). In a random copolymer containing 2 or more of these monomers, the end group is derived from any of the monomers used.

It is preferred that  $a+b+c$  is a minimum of 2 and a maximum such that the molecular weight of the peroxide does not exceed 16,500, and most preferred that  $a+b+c$  is a minimum of 5 and a maximum such that the molecular weight of the peroxide does not exceed 11,000. In all of the formulas in this application a, b and c represent the average number of monomer units in the molecule -- since the poly(perfluoroether)acyl halides are made by polymerization, they have a molecular weight distribution.

Peroxides of this formula can be prepared by reacting a poly(perfluoroether)acyl halide with a peroxide and a base. The poly(perfluoroether)acyl halide is of the formula



wherein

5 Y is a perfluoroalkyl group containing up to 12 carbon atoms,  $a+b+c$  is a minimum of 2 and a maximum such that the maximum molecular weight of the acyl halide is about 16,500;

X is chlorine or fluorine; and

T is  $-CF_2-$  and  $-CF(CF_3)-$ ,  
10 provided that when a is zero, T is not  $-CF(CF_3)-$ , when b is zero T is not  $-CF_2-$ , and further provided that when a and b are both zero, T is  $-CF_2-$ .

Compounds of this type are well known to those skilled in the art, for example, U.S. Patents  
15 3,250,807 and 3,347,901 and J. T. Hill, Journal of Macromolecular Science, Chemistry, vol. A8, pages 499-520 (1974).

The base may be an alkali or alkaline earth metal (bi)carbonate or phosphate. Such weakly basic  
20 anions as carbonates and bicarbonates are preferred. Any metal selected must provide moderate water solubility. The molar ratio of base to acyl halide should be at least 1.

The hydrogen peroxide may contain 16% to 90%  
25 water. Thirty percent hydrogen peroxide is preferred. The ratio of number of moles water/peroxide is about 0.2 to about 10. The preferred ratio is 0.8 to 6. In calculating the ratio of water to peroxide, all water is included  
30 whether introduced in the solvent or as aqueous hydrogen peroxide. The number of moles of peroxide (whether as hydrogen peroxide or another form) should be approximately one-half the molar amount of the poly(perfluoroether)acyl halide (stoichiometrically  
35 equal).



The process can be carried out in the optional presence of a solvent. Inert fluorocarbon fluids are preferred. Especially preferred is 1,1,2-trichlorotrifluoroethane.

The reaction is carried out within a temperature range chosen so that the aqueous phase will not freeze and the peroxide will not decompose. A preferred range is  $-30^{\circ}\text{C}$  to  $40^{\circ}\text{C}$ . The most preferred temperature range is  $-15^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ .

The reaction time may vary from about 1 minute to 8 hours. Preferably the reaction time is about 5 to about 60 minutes. High speed stirring, as with a blender, increases yields.

After the reaction is complete, the reaction mixture may optionally be treated with a solid drying agent (desiccant) to remove water. Anhydrous calcium sulfate (commercially available as Drierite®) is a suitable drying agent. At the same time, it may be convenient to remove insoluble organic salts by filtration, as through glass wool.

The poly(perfluoroether)acyl peroxide may be used as a solution in the solvent in which it was made, or the solvent can be removed (at low temperature, for example by distillation under vacuum) to isolate the peroxide. As in handling peroxides in general, care should be exercised in handling the neat peroxides, especially those of relatively low molecular weight.

These poly(perfluoroether)acyl peroxides are useful as nonvolatile free radical polymerization initiators. They are also useful for preparing free radical polymerized polymers that have a perfluoroether block on one end. Such block polymers are useful for modifying the surface properties of hydrocarbon polymers, as described in European Patent Application 0,161.804.

The poly(perfluoroether)acyl peroxides are also useful for coating solid substrates with fluorocarbon polymers. Such a process comprises:

- (1) coating the solid substrate with a poly(perfluoroether)acyl peroxide; and
- (2) exposing said substrate, coated with said peroxide, to free radical polymerizable fluorocarbon monomers at a temperature at which said peroxide decomposes to form free radicals.

Any convenient method can be used to coat the solid substrate with peroxide, such as dipping into, or brushing or rolling on a solution of the peroxide, and then allowing the solvent to evaporate. Alternatively, the neat peroxide may be brushed or rolled on. Using a solution to do the coating is preferred. Only a minimal amount of peroxide is needed on the solid substrate, since it acts only to initiate the polymerization.

The peroxide coated solid substrate is then exposed to the fluorocarbon monomer at a temperature at which the peroxide decomposes to free radicals, about 10°C to 150°C, preferably 40°C to 80°C. The fluorocarbon monomer can be gaseous, a neat liquid or dissolved in a solvent. Obviously if another liquid such as neat monomer or a solvent is present, the liquid should not appreciably dissolve the peroxide. The thickness of the coating can be controlled by the ratio of surface area of the solid substrate to the amount of fluorocarbon monomer used (area/amount of monomer). The higher this ratio, the thinner the coating.

Fluorocarbon monomers suitable for the coating process are those which contain at least one fluorine atom and may be polymerized by free radicals; such

monomers are well known to those skilled in the art. They include but are not limited to one or more of  
5 tetrafluoroethylene, hexafluoropropylene, perfluoro(2,2-dimethyl-1,3-dioxole), perfluoromethyl vinyl ether, perfluoropropyl vinyl ether, vinylidene fluoride, chlorotrifluoroethylene and vinyl fluoride and copolymers thereof. Tetrafluoroethylene is  
10 preferred. Small amounts, up to 10 mole percent, of free radical polymerizable nonfluorine containing monomers may also be copolymerized into the fluoropolymer coating.

The substrates to be coated can be porous or  
15 nonporous, and include, but are not limited to, fibers, fabrics, paper, metals and ceramics. Preferred substrates are fibers, fabrics and metals. The substrate must be chosen so that the peroxide is stable on the substrate. Some of the transition  
20 metals, especially iron, may cause peroxide decomposition and should be avoided.

In the following Examples, these symbols are used:

A(n) is  $\{CF_3CF_2CF_2O[CF(CF_3)CF_2O]_nCF(CF_3)C(=O)O-\}_2$   
25 B(n) is  $CF_3CF_2CF_2O[CF(CF_3)CF_2O]_nCF(CF_3)C(=O)F$   
The number "n" is the average number of units in the molecule, and is rounded off to the nearest integer.

#### Peroxide Titration

30 The peroxide titration used in the Examples follows. In a loosely stoppered Erlenmeyer flask several grams of dry ice are added to 25 ml of glacial acetic acid, so as to flush oxygen from the system. Five ml of a solution of 30 g of KI in 70 ml  
35 of deoxygenated water is added, and then 5.0 ml of the peroxide solution to be analyzed. The mixture is stirred for 10 minutes to allow the peroxide to react with the iodide. One hundred ml of deoxygenated

water is added and the deep iodine color is titrated to light yellow with 0.1 N sodium thiosulfate. Then  
5 0.5 g of "Thyodene" (from Fisher Scientific Co.)  
iodometric indicator is added making the reaction  
mixture turn blue. Titration is completed by  
bringing to a colorless endpoint with additional  
0.1 N sodium thiosulfate. Molar peroxide  
10 concentration is 0.01 times the total number of ml of  
sodium thiosulfate solution.

#### EXAMPLE 1

##### Preparation of A(8)

15 A flask under a positive pressure of nitrogen  
was loaded with 100 ml of 1,1,2-trichlorotrifluoro-  
ethane and 32 g (0.02 mole) of B(8). The mixture was  
cooled to -5°C and 2.12 g of finely divided sodium  
carbonate (0.02 mole) added. Next 1.0 ml of 30%  
20 hydrogen peroxide (0.01 mole) was added and the  
reaction mixture stirred for 3.5 hours at -5°C under  
a positive pressure of nitrogen. The reaction  
mixture was passed cold through 20 g of Drierite®  
(anhydrous  $\text{CaSO}_4$  desiccant produced by W. A. Hammond,  
25 Drierite Company), 8 mesh, in a chromatography column  
which contained a plug of glass wool in the bottom.  
Addition of 5.0 ml of the reaction mixture to  
potassium iodide in acetic acid/water and titration  
with sodium thiosulfate indicated 0.088 M peroxide.  
30 With no volatile solvent loss and 100% yield, a  
peroxide concentration of 0.083 M would have been  
expected.

#### EXAMPLE 2

##### Preparation of A(60)

35 A flask under a positive pressure of nitrogen  
was loaded with 50 ml of 1,1,2-trichlorotrifluoro-

ethane and 102 g of B(60) (0.005 mole). The mixture was cooled to  $-5^{\circ}\text{C}$  and then 3.26 g of finely divided cesium carbonate (0.01 mole) and 0.50 ml of 30% hydrogen peroxide (0.005 mole) were added. The mixture was stirred for 7 hours at  $0^{\circ}\text{C}$  and then washed through 25 g of Drierite® with an additional 50 ml of 1,1,2-trichlorotrifluoroethane. This mixture was stored in a  $-15^{\circ}\text{C}$  refrigerator where layer separation occurred. The upper layer titrated for no peroxide whereas the lower layer titrated for 0.008 M peroxide. Pure peroxide of 20,000 M. W. and density of 1.9 g/ml would be expected to titrate for 0.095 M peroxide.

### EXAMPLE 3

#### Preparation of A(19)

A flask under a positive pressure of nitrogen was loaded with 50 ml of 1,1,2-trichlorotrifluoroethane and 34 g of B(19) (0.01 mole). The mixture was cooled to  $-5^{\circ}\text{C}$  and then 1.06 g of finely divided sodium carbonate (0.01 mole) and 0.50 ml of 30% hydrogen peroxide (0.005 mole) were added. The mixture was stirred for 30 minutes at  $-5^{\circ}\text{C}$  and then filtered through 50 g of Drierite® into a polyethylene bottle. Peroxide content by titration was 0.05 M. With no volatile solvent loss and 100% yield, a peroxide concentration of about 0.074 M would have been expected.

### EXAMPLE 4

#### Preparation of A(21)

A Waring blender swept with nitrogen and cooled in wet ice was loaded with 200 ml of 1,1,2-trichlorotrifluoroethane, 36.9 g of B(21) (0.01 mole), and

1.05 g of powdered sodium carbonate (0.01 mole). The reaction was stirred briefly and then 0.5 ml of 30% hydrogen peroxide (0.005 mole) added. After stirring for 10 minutes at high speed, the reaction mixture was filtered through 25 g of Drierite®. The filtrate titrated 0.015 M in peroxide. With no volatile solvent loss and 100% yield, a peroxide concentration of 0.023 M would have been expected.

This Example illustrates the advantage of efficient mixing of the water and organic phases.

#### EXAMPLE 5

Preparation of A(19)

A flask was loaded with 50 ml of 1,1,2-trichlorotrifluoroethane and 34 g of B(19) (0.01 mole). The mixture was cooled to -5°C and then 1.06 g of finely divided sodium carbonate (0.01 mole) and 0.135 ml of 90% hydrogen peroxide (0.005 mole) added. The mixture was stirred for 3.5 hours at -5°C and then filtered through 50 g of Drierite® into a polyethylene bottle. Peroxide content by titration was 0.034 M. With no volatile solvent loss and 100% yield, a peroxide concentration of about 0.074 M would have been expected.

#### EXAMPLE 6

Preparation of Peroxide from  $\text{CF}_3\text{O}(\text{CF}_2\text{O})_3\text{CF}_2\text{COF}$

A flask under nitrogen was loaded with 10 g of  $\text{CF}_3\text{O}(\text{CF}_2\text{O})_3\text{CF}_2\text{COF}$  (0.03 mole), 1.59 g of powdered sodium carbonate (0.015 mole), and 100 ml of 1,1,2-trichlorotrifluoroethane. The mixture was cooled to -5°C and then 1.5 ml of 30% hydrogen peroxide (0.015 mole) added. The mixture was stirred for 3 hours at -5°C and then filtered through 20 g

of Drierite® into a polyethylene bottle. Peroxide content by titration was 0.055 M. With no volatile solvent loss and 100% yield, a peroxide concentration of about 0.14 M would have been expected.

#### COMPARATIVE EXAMPLE 1

##### Preparation of A(7)

10 A volumetric flask loaded with 12.25 g of sodium hydroxide was brought to 100 ml with distilled water. This solution (33 ml) was mixed with 100 ml of 1,1,2-trichlorotrifluoroethane and 5.2 ml of 30% hydrogen peroxide at -5°C to -7°C. With rapid stirring, 148 g of B(7) was added over 2 minutes. A mild exotherm raised the reaction mixture to 5°C to 10°C. This mixture was stirred for another five minutes at 0°C. The lower layer carrying a lot of emulsified water was separated with great difficulty. Shaking this layer with the usual aqueous sodium carbonate/bicarbonate wash gave a stiff gel. Freezing the gel and thawing, added hundreds of ml more of 1,1,2-trichlorotrifluoroethane, and forcing through Drierite® gave a small quantity of 0.055 M peroxide solution.

This Example illustrates the problems that excessive amounts of water cause.

#### EXAMPLE 7

30 Coating of Aluminum with Poly(tetrafluoroethylene)  
A 0.12 M solution of A(9) in 1,1,2-trichlorotrifluoroethane was washed down the 1.5 X 4" rectangular face of a 16.18 g grit blasted aluminum coupon. The coupon was dried for 15 minutes under vacuum at room temperature. The coupon now weighed 16.26 g indicating A(9) pickup of 0.08 g. The coupon

was loaded into a 400 ml stainless steel autoclave with 50 g of gaseous tetrafluoroethylene and heated at 60°C for 4 hours. On recovery, the aluminum coupon weighed 17.47 g, the 1.21 g weight gain coming from a visually continuous plastic film of poly(tetrafluoroethylene) covering the grit blasted side of the coupon.

10

#### EXAMPLE 8

##### Coating of Kevlar® Fibers with Poly(tetrafluoroethylene)

A slurry made from 4.29 g of Kevlar® [poly(p-phenylterephthalamide)] fibrils, 5 ml of 0.09 M A(8), and 80 ml of 1,1,2-trichlorotrifluoroethane was stripped to dryness, first using a rotary evaporator, and then a vacuum pump for fifteen minutes. These fibrils were loaded into a 400 ml autoclave with 50 g of gaseous tetrafluoroethylene. Heating for 3 hours at 60°C gave 45.3 g of Kevlar® fibrils coated with poly(tetrafluoroethylene).

20

#### EXAMPLE 9

Coating of Kevlar® Pulp with  
Poly(tetrafluoroethylene/perfluoropropyl vinyl ether)

A slurry was prepared using 25 g of Kevlar® pulp, 10 ml of 0.01 M A(9), and 250 ml of 1,1,2-trichlorotrifluoroethane. This was stripped to dryness, first using a rotary evaporator, and then a vacuum pump for 30 minutes. The pulp was loaded into a 400 ml autoclave along with 50 g of gaseous tetrafluoroethylene and 3 g of gaseous perfluoropropyl vinyl ether. Standing for 24 hours at room temperature gave 51.3 g of pulp coated with copolymer.

30

35



EXAMPLE 10

Coating of Sailcloth with Poly(tetrafluoroethylene)

5       A 3.79 g sample of polyester sailcloth was  
mounted on a frame and rinsed with 1,1,2-trichloro-  
trifluoroethane to clean the surface. The sailcloth  
was then rinsed with 0.025 M A(10) in 1,1,2-trichloro-  
fluoroethane and drained. The sample was transferred  
10   to a 500 ml pressure vessel. The vessel was  
evacuated for 5 minutes to remove residual 1,1,2-tri-  
chlorotrifluoroethane and then pressured with 49 to  
62 psi of tetrafluoroethylene gas. After standing  
overnight at room temperature, the sample was  
15   recovered. The cloth now weighed 6.20 g and was  
covered with a shiny coating of poly(tetrafluoro-  
ethylene).

Although preferred embodiments of the invention  
20   have been described, it is understood that there is  
no intent to limit the invention to the precise  
embodiments described and it is further understood  
that the right is reserved to all changes and  
modifications which fall within the scope of the  
25   claims.

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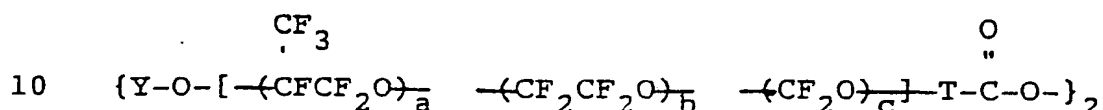
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CLAIMS

What is claimed is:

5

1. A poly(perfluoroether)acyl peroxide of the formula



wherein

Y is a perfluoroalkyl group containing up to 12

15

carbon atoms,  $\text{-(CFCF}_2\text{O)-}$ ,  $\text{-(CF}_2\text{CF}_2\text{O)-}$  and

$\text{-(CF}_2\text{O)-}$  are repeat units where  $a+b+c$  is a minimum of 2 and a maximum such that the maximum molecular weight of the peroxide is about 33,000; and

20

T is  $\text{-CF}_2\text{-}$  and  $\text{-CF(CF}_3\text{)-}$ ,

provided that when a is zero, T is not  $\text{-CF(CF}_3\text{)-}$ , when b is zero T is not  $\text{-CF}_2\text{-}$ , and further provided that when a and b are zero, T is  $\text{-CF}_2\text{-}$ .

25

2. A process for the preparation of polymeric (perfluoroether)acyl peroxide product comprising reaction of an acyl halide with a peroxide, under basic conditions, in the presence of a limited amount of water, wherein the water to peroxide molar ratio is controlled in the starting reaction mixture so that such ratio is from out 0.2 to about 10.

35

3. The process of Claim 2 wherein the reaction mixture is passed through a solid desiccant to remove liquid water, at the conclusion of the reaction process.

4. The process of Claim 3 wherein the desiccant is anhydrous calcium sulfate.

5. The process of Claim 2 wherein the molar ratio of water to peroxide is from about 0.8 to about 6.

6. The process of Claim 2 wherein the base is an alkali or alkaline earth (bi)carbonate or phosphate that is soluble in the reaction mixture.

7. The process of Claim 2 carried out within a temperature range of  $-30^{\circ}\text{C}$  to  $40^{\circ}\text{C}$ .

8. The process of Claim 7 carried out within a temperature range of  $-15^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ .

9. The poly(perfluoroether)acyl peroxide of Claim 1 wherein more than one type of monomer unit is enclosed within the bracketed term.

10. The poly(perfluoroether)acyl peroxide of Claim 9 wherein the polymer is a block copolymer.

11. The poly(perfluoroether)acyl peroxide of Claim 9 wherein the polymer is a random copolymer.

12. The poly(perfluoroether)acyl peroxide of Claim 10 wherein "T" is a fragment of the last monomer used.

13. The peroxide of Claim 1 wherein Y is  
5 CF<sub>3</sub>-, a is zero, b is zero and the repeat unit is  
-CF<sub>2</sub>O-.

14. The peroxide of Claim 1 wherein Y is  
10 CF<sub>3</sub>CF<sub>2</sub>-, T is -CF<sub>2</sub>-, a is zero, c is zero and the  
repeat unit is -CF<sub>2</sub>CF<sub>2</sub>O-.

15. The peroxide of Claim 1 wherein Y is  
15 CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>-, T is -CF(CF<sub>3</sub>)-, b is zero, c is zero and  
the repeat unit is -CF(CF<sub>3</sub>)CF<sub>2</sub>O-.

16. The peroxide of Claim 1 wherein the value  
of a+b+c is a minimum of 2 and a maximum of such that  
the molecular weight of the peroxide does not exceed  
16,500.

20 17. The peroxide of Claim 16 wherein the  
value of a+b+c is a minimum of 5 and a maximum such  
that the molecular weight of the peroxide does not  
exceed 11,000.

25 18. The peroxide of Claim 17 wherein Y is  
CF<sub>3</sub>-, a is zero, b is zero and the repeat unit is  
-CF<sub>2</sub>O-.

30 19. The peroxide of Claim 17 wherein Y is  
CF<sub>3</sub>CF<sub>2</sub>-, T is -CF<sub>2</sub>-, a is zero, c is zero and the  
repeat unit is -CF<sub>2</sub>CF<sub>2</sub>O-.

35 20. The peroxide of Claim 17 wherein Y is  
CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>-, T is -CF(CF<sub>3</sub>)-, b is zero, c is zero and  
the repeat unit is -CF(CF<sub>3</sub>)CF<sub>2</sub>O-.

21. A process for coating solid substrates with fluoropolymers comprising:

5 (1) coating the solid substrate with a poly(perfluoroether)acyl peroxide, forming a coated substrate; and

(2) then exposing said coated substrate to free radical polymerizable fluorocarbon monomers at a  
10 temperature at which said peroxide decomposes to form free radicals so that said monomers are polymerized onto said coated substrates.

22. The process of Claim 21 wherein the  
15 coating of the solid substrate is accomplished by applying to the substrate a solution of peroxide, then evaporating the solvent.

23. The process of Claim 21 wherein the  
20 coating of the solid substrate is accomplished by applying neat peroxide to the substrate surface.

24. The process of Claim 21 wherein the  
temperature at which the coated substrate is exposed  
25 to a free radical polymerizable fluorocarbon monomer is about 10°C to about 150°C.

25. The process of Claim 24 wherein the  
temperature is 40°C to 80°C.

30

26. The process of Claim 21 wherein the fluorocarbon monomers are selected from one or more of perfluoro(2,2-dimethyl-1,3-dioxole), perfluoro-  
methyl vinyl ether, perfluoropropyl vinyl ether,  
35 vinylidene fluoride, chlorotrifluoroethylene and vinyl fluoride.

27. The process of Claim 26 wherein the fluorocarbon monomer is tetrafluoroethylene.

5

28. The process of Claim 21 wherein the free radical polymerizable monomers are copolymerized onto the coated substrate.

10

29. The process of Claim 21 wherein the solid substrate is selected from fibers, fabrics, paper, metals and ceramics.

15

30. The process of Claim 29 wherein the solid substrate is selected from fibers, fabrics and metals.

31. The process of Claim 26 wherein the fluorocarbon monomer is gaseous.

20

32. The process of Claim 26 wherein the fluorocarbon monomer is neat.

33. The process of Claim 26 wherein the fluorocarbon monomer is in solution.

25

34. The process of Claim 21 wherein the peroxide is poly(hexafluoropropylene oxide)acyl peroxide.

30

35. The product of the process of Claim 21.

35

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 90/03077

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC <sup>5</sup> : C 07 C 409/32, C 08 G 65/32, C 08 F 4/34, C 08 F 283/06														
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched <sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%; border-bottom: 1px solid black;">Classification System <sup>1</sup></th> <th style="width: 70%; border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; padding: 5px; vertical-align: top;">IPC<sup>5</sup></td> <td style="border: 1px solid black; padding: 5px; vertical-align: top;">C 08 G, C 08 F, C 07 C</td> </tr> </table> <div style="border-top: 1px solid black; padding-top: 5px; margin-top: 5px;">           Documentation Searched other than Minimum Documentation            to the extent that such Documents are included in the Fields Searched <sup>8</sup> </div>			Classification System <sup>1</sup>	Classification Symbols	IPC <sup>5</sup>	C 08 G, C 08 F, C 07 C								
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category <sup>10</sup></th> <th style="width: 70%; border-bottom: 1px solid black;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 20%; border-bottom: 1px solid black;">Relevant to Claim No. <sup>13</sup></th> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">Y</td> <td style="border: 1px solid black; padding: 5px; vertical-align: top;">           EP, A, 0186215 (DAIKIN INDUSTRIES)            2 July 1986            see page 2, lines 19-26; page 4,            line 19 - page 5, line 7; examples            1-4; claims 1-3,5            --         </td> <td style="border: 1px solid black; text-align: center; vertical-align: top;">1-20</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">Y</td> <td style="border: 1px solid black; padding: 5px; vertical-align: top;">           FR, A, 2107356 (MINNESOTA MINING AND            MANUFACTURING CO.) 5 May 1972            see page 4, line 22 - page 5, line            1; page 6, lines 29-34; example 4;            claims            cited in the application            --         </td> <td style="border: 1px solid black; text-align: center; vertical-align: top;">1-20</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">A</td> <td style="border: 1px solid black; padding: 5px; vertical-align: top;">           Chemical Patents Index, Basic Abstracts            Journal, Section A: PLASDOC, week            8634, 15 October 1986, AN 86-221956/34,            Derwent Publications Ltd, (London,            GB),            &amp; JP, A, 61152653 (DAIKIN KOGYO K.K.)            11 July 1986            see abstract            -----         </td> <td style="border: 1px solid black; text-align: center; vertical-align: top;">1</td> </tr> </table>			Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	Y	EP, A, 0186215 (DAIKIN INDUSTRIES) 2 July 1986 see page 2, lines 19-26; page 4, line 19 - page 5, line 7; examples 1-4; claims 1-3,5 --	1-20	Y	FR, A, 2107356 (MINNESOTA MINING AND MANUFACTURING CO.) 5 May 1972 see page 4, line 22 - page 5, line 1; page 6, lines 29-34; example 4; claims cited in the application --	1-20	A	Chemical Patents Index, Basic Abstracts Journal, Section A: PLASDOC, week 8634, 15 October 1986, AN 86-221956/34, Derwent Publications Ltd, (London, GB), & JP, A, 61152653 (DAIKIN KOGYO K.K.) 11 July 1986 see abstract -----	1
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<sup>10</sup> Special categories of cited documents: <sup>10</sup> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu- ments, such combination being obvious to a person skilled in the art "&" document member of the same patent family													
<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">           Date of the Actual Completion of the International Search            12 octobre 1990         </td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">           Date of Mailing of this International Search Report            09. 11. 90         </td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;">           International Searching Authority            EUROPEAN PATENT OFFICE         </td> <td style="border-bottom: 1px solid black; padding: 5px;">           Signature of Authorized Officer  <div style="text-align: right;">               Nuria TORIBIO           </div> </td> </tr> </table>			Date of the Actual Completion of the International Search 12 octobre 1990	Date of Mailing of this International Search Report 09. 11. 90	International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer <div style="text-align: right;">               Nuria TORIBIO           </div>								
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# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9003077  
SA 38923

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 24/10/90. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0186215	02-07-86	JP-A, B, C 61152652	11-07-86
		US-A- 4654444	31-03-87
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		AU-B- 466474	30-10-75
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		BE-A- 772310	07-03-72
		DE-A, C 2145175	16-03-72
		GB-A- 1358418	03-07-74
		NL-A- 7111816	10-03-72
		US-A- 3882193	06-05-75